

Elaboration of Nanocomposites Based on Poly (Ethyl Methacrylate-co-Acrylonitrile) by in Situ Polymerization Using an Algerian Bentonite. Thermal Stability and Kinetic Study

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This contribution focuses on the synthesis and characterization of nanocomposites based on poly (ethyl methacrylate-co-acrylonitrile) (PEMAN) and different loadings of an organically modified bentonite from Algeria prepared via in situ polymerization.

TEM images and X-ray patterns revealed that depending on the loading of this clay, intercalated or partially exfoliated nanocomposites were obtained. These nanocomposites showed an increase in their glass transition temperature compared to the pure copolymer as investigated by Differential Scanning Calorimetry and improved thermal stability as evidenced by Thermogravimetric analysis and kinetics of their thermal degradation. Activation energies (E_a) of thermal decomposition of PEMAN and its nanocomposites were determined by Flynn–Wall–Ozawa and Kissinger-Akahira-Sunose methods. The changes in (E_a) value with the level of conversion suggest a significant improved thermal stability of the nanocomposites compared to the copolymer matrix.

Keywords: Poly (ethyl methacrylate-co-acrylonitrile), Hexadecyltrimethylammonium chloride, Intercalated, Partially exfoliated nanocomposite, Maghnia bentonite, Kinetic of thermal decomposition.

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1. INTRODUCTION

A very significant number of papers are regularly published in the field of polymer/clay nanocomposites [1-4] using often commercial clays such as cloisites.

In situ polymerization or intercalation from solution methods are among the recommended ways to achieve the best dispersion of clay particles in a polymer matrix since the resulting properties of such nanocomposites prepared accordingly are usually superior to those obtained via melt intercalation.

Although several studies dealt with clay nanocomposites based on copolymers of acrylonitrile and other monomers such styrene, methyl methacrylate or butadiene, to our knowledge, the preparation of nanocomposites based on poly (ethyl methacrylate-co-acrylonitrile) in presence of an Algerian organically modified bentonite, has not been reported.

In this communication, we will report on an attempt to elaborate for the first time, nanocomposites based on ethyl methacrylate and acrylonitrile via in situ free radical polymerization in THF, using AIBN as initiator in presence of different loadings of a bentonite from Algeria, organically modified by hexadecyltrimethylammonium chloride (OMMT).

The structure, morphology and thermal stability of the elaborated materials were investigated in a second step by FTIR, XRD and Transmission electronic microscopy (TEM), DSC and TGA.

In the last part of this contribution, the kinetic parameters of degradation of pure PEMAN and its nanocomposites with different amounts of OMMT, estimated using different methods are presented [5-8].

2. EXPERIMENTAL

2.1 Materials

Ethyl methacrylate and acrylonitrile monomers were purified under reduced pressure. A Bentonite

from Maghnia (Algeria) was kindly supplied by Bentonite Company of Algeria and analyzed by the central laboratory of the ENOF. This clay containing SiO_2 (55 – 65 %), Al_2O_3 (12 – 18 %), Fe_2O_3 (1 – 3 %), Na_2O (1 – 3 %), CaO (1 – 5 %), K_2O (0.76 – 1.75 %) and MgO (2 – 3 %) was purified and organically modified by Hexadecyltrimethylammonium chloride in a similar way as previously reported [9].

2.2 Synthesis

Poly (ethyl methacrylate-co-acrylonitrile) was synthesized by free radical polymerization in THF at 60 °C and 0.1 % by weight of azobis isobutyronitrile (AIBN) as initiator. The copolymer, obtained by precipitation in a large excess of methanol, was purified by repeated dissolution/precipitation, dried in a vacuum oven at 60 °C for several days and characterized by different techniques.

Appropriate amount of OMMT (1, 2 and 4 % by weight) was dispersed in THF under magnetic stirring for 24 hours at room temperature. Similar amounts of ethyl methacrylate and acrylonitrile used to prepare the virgin copolymer were added to the clay suspension and stirred vigorously for another 24 hours. 0.1 % by weight of AIBN was then added to the solution that was maintained at 60 °C for 3 hours under nitrogen atmosphere. The synthesized materials were obtained by precipitation from an excess of methanol, purified and dried under the same conditions than the virgin copolymer.

2.3 Characterizations

The content of acrylonitrile in PEMAN determined using $^1\text{H-NMR}$ performed on a Bruker Advanced spectrometer operating at 200 MHz in CDCl_3 at 25 °C, using tetramethylsilane (TMS) as the internal reference standard, was found to be 20 mol %.

FTIR spectra of thin films of PEMAN and PEMAN/OMMT hybrids, cast from THF solutions onto KBr

disks, were recorded at room temperature on a Perkin-Elmer spectrometer One. 60 scans were signal averaged at a spectral resolution of 2 cm^{-1} .

X-Ray patterns of the elaborated materials were recorded on a Philips PW3710 diffractometer in the range of 2θ ($2-50$). The monochromatic radiation applied was $\text{CuK}\alpha$ ($\lambda = 1.5406\text{\AA}$).

As a complementary technique to XRD, TEM was used to investigate the morphology of the elaborated materials using a JEOL 1400 equipped with a MORADA SIS numerical camera at an acceleration voltage of 120 kV.

The glass transition temperatures (T_g) of the synthesized PEMAN copolymer and its PEMAN/OMMT nanocomposites were determined by differential scanning calorimetry using

Pyriss 1 DSC analyser at $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$.

Experiments of a thermogravimetric analysis were carried out on a TA instruments analyser TGA-Q500 under a nitrogen atmosphere from $30\text{ }^\circ\text{C}$ to $650\text{ }^\circ\text{C}$

Non-isothermal TGA of the samples were performed under nitrogen at constant heating rates of 5, 10, 15 and $20\text{ }^\circ\text{C}\cdot\text{min}^{-1}$.

3. RESULTS AND DISCUSSION

3.1 FTIR

After modification with Hexadecyltrimethylammonium salt, the spectrum of OMMT shows additional absorption peaks at 1473 , 2922 and 2850 cm^{-1} assigned to the (C-H) and (-CH₂-) stretching vibration.

FTIR spectra of pure bentonite (MMT), organically modified bentonite (OMMT), (PEMAN) copolymer and its (PEMAN/OMMT) materials show the characteristic bands of pure bentonite at 462 cm^{-1} , 524 cm^{-1} and 1038 cm^{-1} , additional bands at 1473 cm^{-1} , 2850 cm^{-1} and 2922 cm^{-1} , indicating that intercalation of the alkyl-ammonium ions within the interlayer spacing of the bentonite and peaks at 2240 cm^{-1} and 1728 cm^{-1} confirming the presence of acrylonitrile and ethyl methacrylate moieties of PEMAN respectively.

3.2 X-ray diffraction

X-Ray diffraction patterns of pure (MMT), organically modified bentonite (OMMT), PEMAN and of typical PEMAN/OMMT nanocomposite are illustrated in Fig. 1. The characteristic peak of MMT observed at $2\theta = 6.40^\circ$, corresponding to a d-spacing of 1.38 nm , shifted to a lower angle of 5.80° with OMMT increasing the d-spacing to 1.52 nm and indicated the intercalation of the Hexadecyltrimethylammonium ion into the layer of this clay. A relatively narrow and intense peak observed at $2\theta = 4.00^\circ$ corresponds to a d-spacing of 2.20 nm and a small shoulder corresponding to a d-spacing of 3.20 nm with PEMAN/OMMT prepared in presence of 2 % by weight of OMMT. The diffractogram of PEMAN/OMMT (1wt %) showed a diffraction peak at $2\theta = 2.40^\circ$, corresponding to a d-spacing of 3.67 nm . These observations indicate the formation of intercalated nanocomposites.

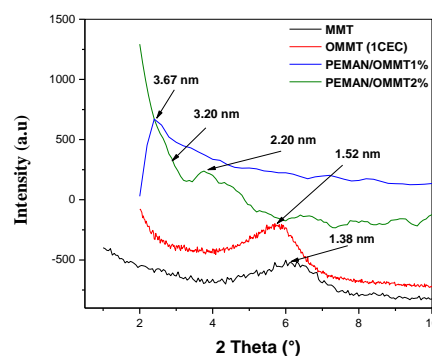


Fig. 1 – X-Ray diffraction patterns of MMT, OMMT PEMAN and PEMAN/OMMT (1 and 2w %)

3.3 TEM

In order to confirm the nanocomposite structure, the dispersion of OMMT in PEMAN/OMMT was investigated by TEM. Typical TEM micrograph of PEMAN/OMMT (2 %), illustrated in Fig. 2 confirmed in agreement with XRD the formation of mixed intercalated/exfoliated nanocomposite structures evidenced at high magnification by the presence of stacked layers randomly dispersed in the copolymer matrix of relatively small dimensions with thickness ranging from 8 to 25 nm and a length varying between 60 to 180 nm. Some individual exfoliated silicate sheets are also shown. Although only a diffraction peak of very small intensity was observed at around $2\theta = 2.4^\circ$ with PEMAN/OMMT containing 1 % of OMMT, a higher number of stacks of a smaller thickness varying between 4 and 14 nm and an average d-spacing larger than 3.5 nm were confirmed by TEM as shown in Fig. 3 with PEMAN/OMMT containing 1 % of OMMT and indicating the presence of more exfoliated structures. TEM images also confirmed the presence of some weakly intercalated stacks of much larger thickness.

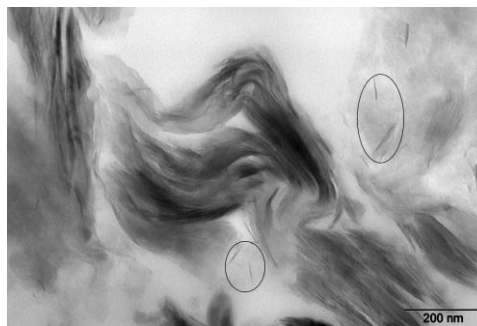


Fig. 2 – TEM micrograph of PEMAN/OMMT 2wt % material

3.4 DSC analysis

DSC analysis showed an increase in T_g , of $8\text{ }^\circ\text{C}$ compared to the virgin PEMAN, observed with the nanocomposite prepared with 1wt % of OMMT.

3.5 TGA Analysis

Fig. 3 shows the TG and respective derivative curves of PEMAN and selected binary nanocomposites under nitrogen.

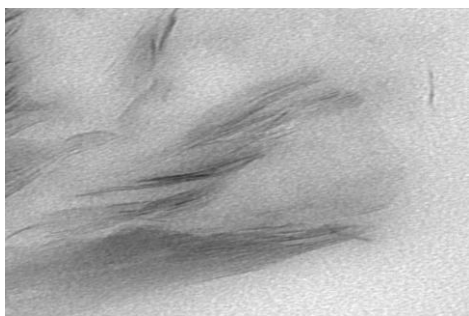


Fig. 3 – TEM image of PEMAN/OMMT 1 % material

The onset temperature $T_{10\%}$ (temperature at 10% mass loss) and the temperature at 50% mass loss ($T_{50\%}$) of the nanocomposites (2 and 4wt %) increased as compared to the virgin PEMAN while PEMAN/OMMT (1wt %) lost a significant amount of its salt in this temperature range. This improvement in thermal stability of PEMAN nanocomposites is mainly due to the intercalation of polymer matrix into the clay galleries, which act as a barrier for thermal degradation. The degradation temperature at maximum T_{max} increased by 12°C for the nanocomposite of partially exfoliated structure and decreased with an increase of OMMT amount as shown in Fig. 4.

We have in the present investigation, in order to estimate the kinetic parameters of degradation of pure PEMAN and its nanocomposites with different amounts of OMMT, used, Flynn–Wall–Ozawa (FWO) and Kissinger–Akahira–Sunose (KAS) methods [5-8].

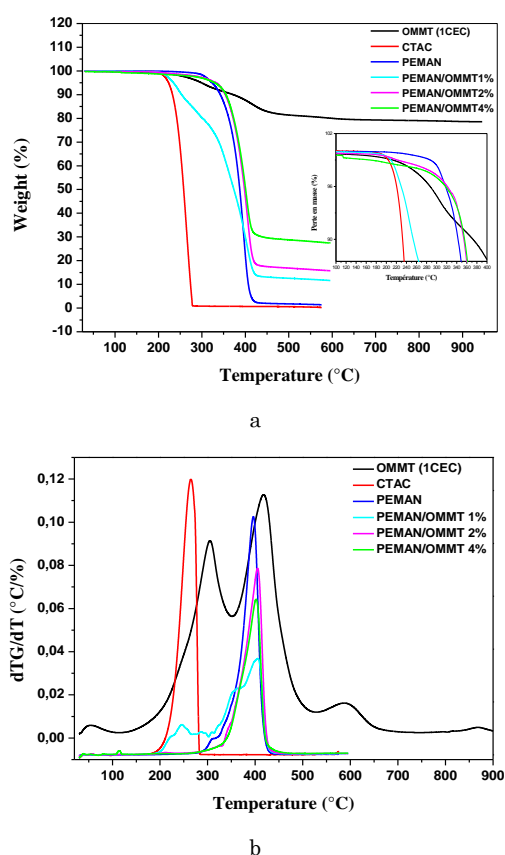


Fig. 4 – TG (a) and d(TG) (b) thermograms of OMMT, CTAC, PEMAN and PEMAN/OMMT(1, 2 and 4wt %)

Non-isothermal TGA of the different materials were performed under nitrogen at constant heating rates of 5, 10, 15 and 20 °C.min⁻¹. The TGA and dTG curves for the decomposition of PEMAN copolymer and of selected PEMAN/OMMT nanocomposites at different heating rates using the selected Flynn-Wall-Ozawa method are shown in Fig. 5. It can be clearly observed from this figure that the thermogram shifts towards higher temperature as the heating rate increases.

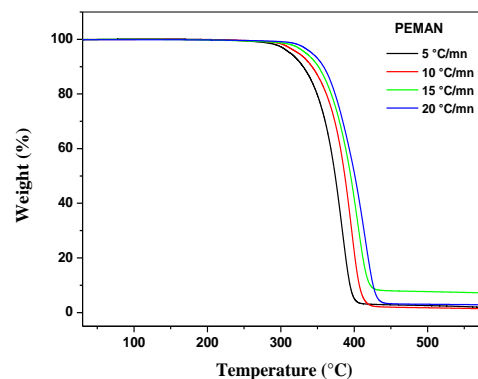


Fig. 5 – Thermograms of PEMAN at different degradation rates (5, 10, 15 and 20 °C/mn)

The activation energies E_a estimated using the Flynn–Wall–Ozawa (FWO) and the Kissinger–Akahira–Sunose (KAS) described by equations 1 and 2 below:

$$\log \beta = \left[\log \frac{A E_a}{R} - \log f \alpha - 2.315 \right] - 0.4567 \frac{A E_a}{R},$$

$$\log \beta / T^2 = \ln \left[\frac{A R}{E_a} g \alpha \right] - E_a / R T,$$

where β is the constant heating rate (dT/dt), E_a is the activation energy, T the absolute temperature (in K), α is the conversion (weight of materials volatilized/initial weight of materials) and R is the gas constant.

The activation energies E_a of degradation calculated from the slope of the $\log \beta$ or $\ln (\beta/T^2)$ versus $1/T$ plots are shown in Fig. 6 and Fig. 7.

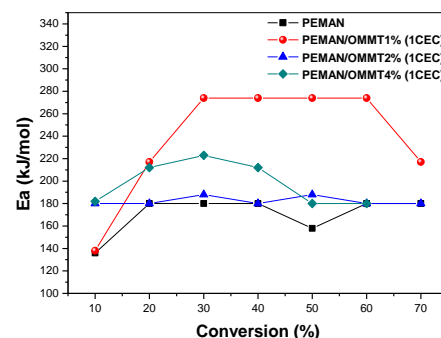


Fig. 6 – Variation of the activation energy versus conversion using Ozawa's method for PEMAN and its PEMAN/OMMT nanocomposites

It is evident that the activation energies of degradation for these samples remain relatively constant after 20–30 % conversion, which reveals that up to 20 or 30 % conversion there is one dominant kinetic process.

There is a clear trend between the activation energy

of degradation and the OMMT content of these samples. The activation energy values for 2wt % PEMAN/OMMT nanocomposites are higher than those of neat PEMAN, and increase with increasing the content of OMMT. Higher activation energies were obtained with PEMAN/OMMT (1wt %).

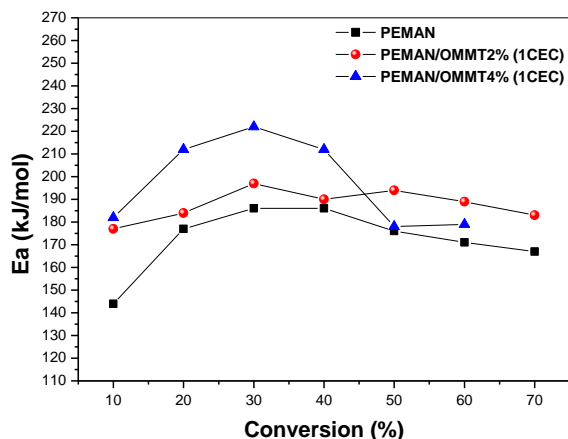


Fig. 7 – Variation of the activation energy versus conversion using KAS method for PEMAN and its PEMAN/OMMT nanocomposites

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4. CONCLUSIONS

This study showed, for the first time, that intercalated and partially exfoliated nanocomposites based on ethyl methacrylate and acrylonitrile copolymer were successfully prepared by in situ polymerization, using a bentonite from Maghnia (Algeria), modified by hexadecyltrimethylammonium chloride and THF as solvent.

The intercalated and partially exfoliated structures of the elaborated nanocomposites exhibited an overall improved thermal stability investigated by TGA and an increase in T_g compared to the virgin copolymer.

Nanocomposites prepared with 1 % by weight of OMMT were of partially exfoliated structure and led to the highest T_g and to the highest degradation temperature at maximum.

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